

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : C08G 63/06, 69/08	A1	(11) International Publication Number: WO 92/08749 (43) International Publication Date: 29 May 1992 (29.05.92)
(21) International Application Number: PCT/US91/07975 (22) International Filing Date: 28 October 1991 (28.10.91) (30) Priority data: 615,398 19 November 1990 (19.11.90) US 763,322 20 September 1991 (20.09.91) US (71) Applicant: CORNELL RESEARCH FOUNDATION, INC. [US/US]; Cornell Business and Technology Park, Suite 105, 20 Thornwood Drive, Ithaca, NY 14850 (US). (72) Inventors: FRECHET, Jean, M., J. ; 25 Fairway Drive, Ithaca, NY 14850 (US). HAWKER, Craig, J. ; 210 Lake Street, Ithaca, NY 14850 (US). UHRICH, Kathryn ; 304 East Falls Road, Ithaca, NY 14850 (US).		(74) Agents: WINTER, Richard, C.; PCT International, Inc., P.O. Box 573, New Vernon, NJ 07976 (US) et al. (81) Designated States: AT (European patent), BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: HYPERBRANCHED POLYESTERS AND POLYAMIDES (57) Abstract Hyperbranched polyester and polyamide polymers are prepared by a one-step process of polymerizing a monomer of the formula A-R-B ₂ so that high molecular weight globular polymers having a multiplicity of a particular functional group on the outside surface are obtained.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LI	Liechtenstein	SU ⁺	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TC	Togo
DE*	Germany	MC	Monaco	US	United States of America
DK	Denmark				

⁺ Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

HYPERBRANCHED POLYESTERS AND POLYAMIDES

Background of the Invention

The present invention is directed to the preparation of high molecular weight hyperbranched polyester and polyamide polymers. The polymers are produced by a one-step process which entails polymerizing specific monomers of the formula $A-R-B_2$ in such a manner that side-reactions, i.e. reverse reactions, isomerization, crosslinking, and the like are substantially avoided.

P.J. Flory, J. Am. Chem. Soc., 74, 2718 (1952) and Principles of Polymer Chemistry, Cornell University Press, 1953, pp. 361-70, discusses the theory of condensation polymerization of so-called AB_n -type monomers wherein A and B functions condense together to form branched polymers. While theoretically such polymers should be of high molecular weight, such has not been the case in actual practice. The only specific disclosures of such polymers are obtained by (i) the Friedel-Crafts condensation of benzyl halides in the presence of a MX_3 catalyst wherein X is a halogen, (ii) the elimination metal halides from alkali metal salts of trihalophenols, and (iii) intermolecular etherification of D-glucose in the presence of dilute acids to form a soluble polyglucose. Hyperbranched polyester and polyamide polymers are not disclosed. Also, only low molecular weight polymers, i.e. less than about 1,000 daltons, were obtained.

A recent attempt at producing a poly(arylene)polymer by following Flory's theory has also resulted in a polymer having a number average molecular weight below 10,000. Kim et al., J. Am. Chem. Soc., 1990, 112, 4592-3, and Kim U.S. Patent No. 4,857,630 disclose wholly aromatic poly(arylene) polymers prepared by the homocoupling of (3,5-dibromophenyl)boronic acid in a mixture of an organic solvent and aqueous sodium carbonate along with a palladium-containing catalyst. The molecular weight of the polymer was found to depend on the organic sol-

vent and temperature employed during polymerization and addition of additional monomer at the end of the polymerization neither increased the molecular weight nor gave a bimodal distribution. Kim et al. could not explain what causes the molecular growth of the system to stop. Only low molecular weight polymers, i.e. about 5,000 daltons, were produced. During the polymerization, only single bonds between arylene groups are formed and no polyester or polyamide polymers are disclosed or suggested.

Baker et al. U.S. Patent No. 3,669,939 discloses condensation polymerizing other ARB_2 monomers, i.e. polyhydroxymonocarboxylic acid aliphatic compounds, but only succeeds in generating polymers with molecular weights below 4,000 daltons. While the molecular weights obtained in Baker et al. are not provided, the acid values which are provided permit the calculation thereof.

In view of the previous inability to directly prepare high molecular weight hyperbranched polymers in accordance with Flory's theory, the art is replete with multi-step procedures attempting to accomplish a similar result. For instance, Tomalia et al. U.S. Patent Nos. 4,507,466, 4,558,120, 4,568,737, 4,587,329, and 4,737,558 disclose dense "starburst" polymers produced by allowing a polyfunctional amide core molecule to react with excess methyl acrylate in a Michel-type addition. Each arm of the resulting star-branched molecule is then reactivated to an amine-terminated moiety by exhaustive amidation using excess 1,2-diaminoethane to afford a chain extended product in which each primary amino group becomes a new branch point in the next series of Michael additions. The polymers are thus built up, layer after layer, from a core substance by selective condensation of functional groups with each successive layer becoming a core for the subsequent layer. Only aliphatic polyamides and polyethers are exemplified and the monomers used are of the A-B type.

Similarly, Denkewalter et al. U.S. Pat. Nos. 4,289,872,

4,360,646 and 4,410,688 disclose highly branched polyamide polymers produced from lysine - an A-R-B₂ monomer having one carboxy group, two amino groups, and an aliphatic body - but utilizes a multi-step process of blocking the functional groups and then unblocking them. Only relatively low molecular weight polymers were produced due to the inherent difficulty in obtaining complete reaction for each of the multiple of blocking, unblocking, and reacting steps.

Extensive prior art exists on the preparation of linear aromatic polyesters derived from, for example, 4-hydroquinone and phthalic acid or derivatives thereof. Also, Kricheldorf et al., Polymer Bulletin 1, 383-388 (1979) discloses preparing linear aromatic polyesters by heating trimethylsilyloxybenzoyl chloride to greater than 150°C. Kricheldorf et al., Polymer, 23, 1821-29 (1982) discloses forming predominantly aromatic polyesters from 3-trimethylsilyloxybenzoyl chloride and incorporating small amounts, i.e. 0.6 to 16.6 mole %, of 3,5-bis(trimethylsilyloxy)benzoyl chloride to produce a few branch points. The polyesters so formed behave as predominantly linear polymers since they contain only a few potential branches while the present high molecular weight hyperbranched polyesters behave much more like individual particles.

Accordingly, the art has failed to teach a method which succeeds in producing high molecular weight hyperbranched aromatic polyester and polyamide polymers and it is an object of the present invention to produce such polymers to take advantage of their unique properties, i.e. of high polarity, low crystallinity, and lower than usual viscosity.

Summary of the Invention

The present invention provides soluble hyperbranched aromatic polyester or aromatic polyamide polymers having at least 40% branching and a molecular weight of at least 10,000 and 1,000 daltons respectively, as determined by gel permeation chromatography with polystyrene calibration.

Description of the Preferred Embodiments

The soluble hyperbranched polymers of the present invention are derived from monomers of the formula $A-R-B_2$ in which R is or contains an aromatic moiety and A and B are reactive groups that (i) can take part in either an esterification reaction or an amidation reaction and (ii) yield a by-product which is gaseous at the conditions of the reaction.

Suitable aromatic moieties R for use herein include phenyl, naphthyl, bi-phenyl, diphenyl ether, diphenyl sulfone, benzophenone, and the like.

Suitable A and B groups for use in preparing the hyperbranched polyesters include trialkylsilyloxy and acid halide wherein the alkyl groups contain about 1 to 4 carbon atoms and the halide is chloride, bromide, or fluoride. Specific such monomers include 3,5-bis(trimethylsilyloxy)benzoyl chloride, 5-trimethylsilyloxy-isophthaloyl dichloride, 3,5-bis(triethylsilyloxy)benzoyl chloride, 3,4-bis(trimethylsilyloxy)benzoyl fluoride, 2,4-bis(triethylsilyloxy)benzoyl bromide, and the like in which the benzoyl group is replaced with other aromatic moieties such as those above.

Suitable A and B groups for use in preparing the hyperbranched polyamides include trialkylsilylamino and acid halide wherein the alkyl groups contain about 1 to 4 carbon atoms and the halide is chloride, bromide, or fluoride. Specific such monomers include 3,5-bis(trimethylsilylamino)benzoyl chloride, 5-trimethylsilylamino-isophthalamino dichloride, 3,5-bis(triethylsilylamino)benzoyl chloride, 3,4-bis(trimethylsilylamino)benzoyl fluoride, 2,4-bis(triethylsilylamino)benzoyl bromide, and the like in which the benzoyl group is replaced with other aromatic moieties such as those above.

The condensation polymerization of the $A-R-B_2$ monomer is preferably performed neat, i.e. in the absence of any solvent, since the presence of a solvent has been found to substantially reduce the molecular weight of the resulting hyper-

branched polymer. The polymerization rapidly occurs by heating the monomer to an elevated temperature at which reaction between A and B will occur. The temperature must not be so high as to cause either monomer or polymer decomposition or degradation. Generally a temperature of about 150 to 300°C. will be suitable with the lower temperatures currently preferred for producing higher molecular weight polymers.

The hyperbranched polymers produced herein contain only four different structural units. The first unit is a "focal unit" in which the A group is unreacted and both B groups have reacted. Only a single "focal unit" is present in a polymer molecule. The second unit is a "dendritic repeating unit" in which the A group and both B groups have reacted to form ester or amide linkages. The third unit is a "half-reacted repeating unit" in which the A group and only one of the B groups have reacted while the other B group is unreacted and results in a termination point. The "half-reacting repeating units" reduce the overall degree of branching of the hyperbranched polymer while also contributing to overall growth and the unusual properties of the hyperbranched polymer. The fourth unit is the "terminal unit" in which the A group has reacted but neither of the B groups has reacted.

In the final polymer, it will be quite common for the work-up thereof to hydrolyze or otherwise change the unreacted groups to such as -OH, simple alkoxy groups, or carbamate. Alternatively, after polymerization is complete and before work-up, the hyperbranched polymer may be reacted with a monosubstituted polymer chain terminating compound of the formula $Y-R^1-A$, wherein Y is hydrogen or any functional group which is unreactive under the conditions of the polymerization, R^1 is any aliphatic or aromatic moiety, and A is as defined above. Examples of suitable Y groups include such as ester, cyano, ketone, halide, nitro, amide, thioether, sulphonic ester, alkoxy, and the like. Thus, the outer surface of the globular polymer has a multiplicity of a single functional group.

The degree of branching (DB) of the hyperbranched polymers may be determined by the following formula:

$$DB = \frac{(\# \text{ of dendritic repeating units}) + (\# \text{ of terminal units}) + 1}{\text{total } \# \text{ of units}}$$

wherein the 1 is for the single focal unit since it also contributes to overall branching. As such, the DB must be equal to or less than 1. The % branching is merely DB x 100.

The hyperbranched polymers of this invention have a % branching of at least 40%, preferably at least 50%. The % branching for a particular polymer may be controlled. To increase it, for example, a polyfunctional core molecule containing more than two B groups can be used to initiate growth and control subsequent growth; the monomer unit can be added slowly to the reaction mixture rather than all being present initially; different reaction conditions can be used; fluoride ion activation with such as CsF, KF, or (n-butyl)₄NF as sources of fluoride ion; or the like. To decrease the % branching, small amounts of an A-R-B monomer or a chain terminating compound as described above may be added before or during the polymerization. Generally, however, as high a % branching as possible will be preferred with the theoretical maximum being 100%, though generally the % branching rarely exceeds about 80%.

The molecular weight of the hyperbranched polyester polymers is at least 10,000 daltons and the molecular weight of the hyperbranched polyamide polymers is at least 1,000 daltons, both as determined by gel permeation chromatography with polystyrene calibration. The molecular weight of the polyester polymers is preferably at least 20,000 daltons; more preferably at least about 40,000; and still more preferably from about 40,000 to about 200,000 or more daltons. The molecular weight of the polyamide polymers is preferably from about 1,000 to about 50,000 or more daltons. In view of the reporting of polystyrene equivalent weights, the actual molecular weight of the polymers may in fact be substantially different

from these values. Also, in view of the molecular weights depending upon the specific aromatic groups present, the above numbers may need to be adjusted for other than simple benzoyl groups.

The hyperbranched polyester or polyamide polymers have a generally globular shape with a substantial number of hydroxyl, amino, carboxylic acid or ester groups located at the outer surface of the globules. The presence of the multiplicity of a single type functional group contributes to the usefulness of the hyperbranched polymers. For instance, when the groups are polar hydroxyl groups, the polymers are particularly useful in coatings since their adhesion to polar surfaces is enhanced over less functional materials. And when the groups are carboxylic acid, they can be transformed to ionic carboxylate units in basic medium to form a dendritic ionomer which will be useful in aqueous medium in coatings, additives, high resistance waxes, rheology control additives, and the like. In addition, the hyperbranched polymers exhibit very low crystallinity, very low compressibility, and a lack of shrinking.

The hyperbranched polymers also exhibit a substantially lower than usual viscosity for such high molecular weight polymers. This is in sharp contrast to the higher viscosity observed with conventional linear and normal lightly branched polyesters and polyamides of lower molecular weight. Accordingly, the hyperbranched polymers are particularly useful in both high solids-contents and dry coatings. Also, due to the fully aromatic structures, the polymers possess high thermal stability.

In addition, the hyperbranched polyester and polyamide polymers are expected to be useful in blends, as rheological modifiers, as stiffening agents, and the like, either alone or in combination with linear and/or lightly branched polyesters, polyamides, polycarbonates, polyphenylene oxides, and the like.

In the following non-limiting examples, all parts and percents are by weight unless otherwise specified.

EXAMPLE I

Preparation of Trimethylsilyl 3,5-bis(trimethylsilyloxy)benzoate

To a solution of 3,5-dihydroxybenzoic acid (50.0 g, 0.32 mol) and trimethylsilyl chloride (113 g, 1.04 mol) in dry toluene (500 ml) was added dropwise triethylamine (108 g, 1.07 mol). The mixture was then heated at reflux for 3 hours under nitrogen, cooled, filtered and evaporated to dryness. The crude product was purified by distillation and the fraction boiling at 179-190°C. (0.3 mm) was collected. The trimethyl silyl ester was obtained as a colorless oil (111 g, 90%).

Preparation of 3,5-bis(trimethylsilyloxy)benzoyl chloride

To a solution of trimethylsilyl ester (42.0 g, 114 mmol) in dry dichloromethane (60 ml) containing trimethylammonium chloride (190 mg, 1.2 mmol) was added freshly distilled thionyl chloride (16.2 g, 136 mmol) dropwise under nitrogen. After the addition was complete, the solution was heated at reflux for three hours, cooled, and evaporated to dryness at room temperature. The crude product was purified by short path distillation at 175°C. (0.3 mm) to give the acid chloride as a pale yellow oil (20.6 g, 65%).

Polymerization of 3,5-bis(trimethylsilyloxy)benzoyl chloride

The purified acid chloride (6.0 g, 19.0 mmol) was heated with stirring under nitrogen in an oil bath at 200°C. for one hour. Vigorous effervescence was observed initially and the reaction mixture solidified after about 30 minutes. After cooling, the residue was dissolved in the minimum amount of pyridine/benzene (1:1, ca. 10 ml) at 50°C. and precipitated into methanol (ca 1000 ml). The precipitated polymer was collected by filtration and dried at 80°C. under high vacuum for 3 days and was obtained as a light brown solid (91% yield). Gel permeation chromatology (with polystyrene calibration) showed that the polymer thus obtained had a weight-average molecular

weight M_w of approximately 150,000 and a polydispersity of 3.0. The % branching was 55%.

EXAMPLE II

The procedure of Example I was repeated except that the polymerization was conducted at 250°C. Vigorous effervescence was observed initially and the reaction mixture solidified after ca. 15 minutes. After cooling the residue was dissolved in the minimum amount of pyridine/benzene (1:1, ca. 10 ml) at 50° C. and precipitated into methanol (ca 1000 ml). The precipitated polymer was collected by filtration and dried at 80° C. under high vacuum for 3 days and was obtained as a light brown solid (80% yield). The polymer thus obtained had a M_w of ca. 50,000 (by GPC with polystyrene standards) and a polydispersity of 2.0). The % branching was 55%.

COMPARATIVE EXAMPLE A

The procedure of Example I was repeated except that (i) the purified acid chloride (5.0 g) was dissolved in 1,2-dichlorobenzene solvent (15 ml) prior to commencing the polymerization and (ii) the polymerization was conducted at the reflux temperature of the solvent, 180°C. The resultant polymer was found to have a molecular weight of only about 3,000 (by GPC with polystyrene standards) with about 50% branching.

COMPARATIVE EXAMPLE B

The procedure of Example I was repeated except that the acid chloride was not purified by the short path distillation before polymerization was attempted. The subsequent polymerized material was insoluble and thus no data could be obtained. It was discarded.

COMPARATIVE EXAMPLE C

The purified acid chloride (6.0 g, 19.0 mmol) of Example I was dissolved in dry tetrahydrofuran (THF) solvent (10 ml) and added dropwise to a solution of tetra-n-butylammonium fluoride (1 M sol in THF, 39.0 ml, 39.0 mmol). After stirring at room temperature for 30 minutes, the reaction mixture,

which contained a heavy precipitate, was evaporated to dryness and redissolved in methanol (20 ml). The polymer was then precipitated from the methanol solution into a 1:1 mixture of conc. HCl and water. The precipitated polymer was collected by filtration and dried at 80°C. under high vacuum for 3 days. It was obtained as a light brown solid (91% yield). Gel permeation chromatography (with polystyrene calibration) showed the polymer to have a weight-average molecular weight of about 7,000 and a polydispersity of 1.35. The % branching was 50%.

Claims:

1. A hyperbranched polyester polymer characterized in that it contains aromatic rings, has a molecular weight of at least about 10,000 daltons as determined by gel permeation chromatography with polystyrene calibration, has at least 40% branching, and is prepared by a condensation polymerization of a monomer of the formula $A-R-B_2$ wherein (i) R contains an aromatic moiety and (ii) A and B are chemical moieties which are reactive with each other to form an ester linkage in an esterification reaction.

2. The polymer of Claim 1 characterized in that the aromatic moiety is selected from the group consisting of phenyl, naphthyl, bi-phenyl, diphenyl ether, diphenyl sulfone, and benzophenone.

3. The polymer of Claim 1 characterized in that a monomer of the formula $A-R-B$ is copolymerized with the $A-R-B_2$ monomer.

4. The polymer of Claim 1 characterized in that a polyfunctional core monomer having more than two B groups is copolymerized with the $A-R-B_2$ monomer.

5. The polymer of Claim 1 characterized in that the esterification reaction generates a gaseous by-product.

6. The polymer of Claim 1 characterized in that the reaction generates a gaseous by-product.

7. The polymer of Claim 1 characterized in that A is trialkylsilyloxy wherein the alkyl groups contain about 1 to 4 carbon atoms and B is an acid halide wherein the halide is chloride, bromide, or fluoride.

8. The polymer of Claim 1 characterized in that B is trialkylsilyloxy wherein the alkyl groups contain about 1 to 4

carbon atoms and A is an acid halide wherein the halide is chloride, bromide, or fluoride.

9. The polymer of Claim 1 characterized in that the monomer is a bis(trimethylsilyloxy)benzoyl chloride.

10. The polymer of Claim 1 characterized in that the monomer is 3,5- bis(trimethylsilyloxy)benzoyl chloride.

11. A hyperbranched aromatic polyester polymer having a molecular weight of at least about 10,000 daltons as determined by gel permeation chromatography with polystyrene calibration and having at least 40% branching.

12. A hyperbranched aromatic polyamide homopolymer having a molecular weight of at least about 1,000 daltons as determined by gel permeation chromatography with polystyrene calibration and at least 40% branching and prepared by a bulk condensation polymerization of a monomer of the formula $A-R-B_2$ wherein (i) R is an aromatic moiety and (ii) A and B undergo an amidation reaction at a temperature of about 150 to 300°C. which generates a gaseous by-product.

13. The polymer of Claim 12 wherein R is selected from the group consisting of phenyl, naphthyl, bi-phenyl, diphenyl ether, diphenyl sulfone, and benzophenone.

14. The polymer of Claim 12 wherein A or B is trialkylsilylamino wherein the alkyl groups contain about 1 to 4 carbon atoms and the other of A or B is an acid halide wherein the halide is chloride, bromide, or fluoride.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 91/07975

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)⁶

According to International Patent Classification (IPC) or to both National Classification and IPC
 Int.C1.5 C 08 G 63/06 C 08 G 69/08

II. FIELDS SEARCHED

Minimum Documentation Searched⁷

Classification System	Classification Symbols
Int.C1.5	C 08 G

Documentation Searched other than Minimum Documentation
 to the Extent that such Documents are Included in the Fields Searched⁸

III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹

Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	Polymer, volume 23, no. 12, November 1982, Butterworth and Co. (Publishers) Ltd; H.R. Kricheldorf et al.: "New polymer syntheses: 6*. Linear and branched poly(3-hydroxy-benzoates), pages 1821-1829, see pages 1821-1822; pages 1827-1829 (cited in the application) ---	1-3,5- 11
Y	---	4
P,X	J. Am. Chem. Soc., volume 113, no. 12, 5 June 1991, American Chemical Society,; C.J. Hawker et al.: "One-step synthesis of hyperbranched dendritic polyesters", pages 4583-4588, see the whole article ---	1-3,5- 11
A	US,A,3669939 (A.S. BAKER et al.) 13 June 1972, see column 1, line 45 - column 3, line 46; example 1 (cited in the application) --- -/-	1-6

¹⁰ Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
28-02-1992	27 MAR 1992
International Searching Authority	Signature of Authorized Officer
EUROPEAN PATENT OFFICE	MISS T. TAZELAAR

III. DOCUMENTS CONSIDERED TO BE RELEVANT

(CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
P,Y	WPIL=91-266571, & US, A, 5041516 (CORNELL RES. FOUNDATION) 20 August 1991, see the whole abstract ---	4
A	US,A,2341611 (M. HAGEDORN et al.) 15 February 1944, see the whole document ---	12,13
A	US,A,4568737 (D.A. TOMALIA) 4 February 1986, see column 3, line 1 - column 4, line 32; column 7, line 56 - column 13, line 20 (cited in the application) -----	12

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9107975

SA 53815

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 19/03/92
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3669939	13-06-72	BE-A- 768607	16-12-71
		CA-A- 941994	12-02-74
		DE-A- 2129994	27-01-72
		FR-A, B 2095288	11-02-72
		GB-A- 1325927	08-08-73
		NL-A- 7107945	20-12-71
		SE-B- 367641	04-06-74

US-A- 2341611		None	

US-A- 4568737	04-02-86	US-A- 4507466	26-03-85
		US-A- 4587329	06-05-86
		AU-B- 560604	09-04-87
		AU-A- 2435484	02-08-84
		CA-A- 1244586	08-11-88
		EP-A- 0115771	15-08-84
		WO-A- 8402705	19-07-84
		US-A- 4558120	10-12-85
		US-A- 4631337	23-12-86
US-A- 4737550	12-04-88		
